

# Peierls Instability and Electron-Phonon Coupling in a One-dimensional Sodium Wire

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We have studied Peierls instability in an atomically thin wire of sodium atoms using first-principles density-functional methods. A Na wire has a stable uniform linear structure over a range of inter-atomic distances. At smaller inter-atomic distances it develops a zigzag distortion. At larger inter-atomic distances, just before breaking, a Na wire undergoes a very weak Peierls dimerization. This behavior of a Na wire is understood in terms of its electron-phonon coupling properties.

Fabrication of atomically thin stable wires of gold, and subsequently those of other 5d elements [1, 2] have been major breakthroughs in nanoscience. From the point of view of applications, a striking feature of these nanowires has been an exact quantization of conductance in units of the fundamental conductance  $2e^2/h$  [1]. Some recent experiments have even measured conductances that are fractions of the fundamental unit [3, 4]. These nanowires hold promise for very useful applications in nano-electronics and nanotechnology. They also provide a testing ground for theoretical ideas that have been around for many years now.

One such important idea is due to Peierls. Peierls argued that a one dimensional (1D) metallic system, with one valence electron per atom, will always gain energy by a dimerization of two successive atoms in the wire [5]. Such a dimerization creates a potential at a wavevector  $2k_F$ , and this opens up a gap in the electronic energy bands. Thus a 1D metallic system is doomed to transform into a Peierls insulator (PI). There are many systems, such as MX chains, conjugated polymers, charge-transfer salts in which Peierls instability plays a major role in determining their electronic properties [6]. For systems with bands that are not exactly half-filled, more complex distortions have been observed, including simultaneous existence of two different Peierls-like distortions in Au wires on the Si(553) surface [7].

First-principles calculations of possible Peierls instabilities in 1D metallic systems have

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not always produced conclusive answers. In an earlier work on Al wires, this author could not confirm the existence of a Peierls distorted ground state. Later, Ono and Hirose [8] found a spin-Peierls ground state with a six-atom unit cell for a 1D Al wire in the regime of large inter-atomic distances, a regime which was not considered in Ref. [9]. Studies on gold wires have also been performed. Okamoto and Takayanagi [10] found that at large inter-atomic spacings, a dimerized structure is favored even for a finite Au wire suspended between two electrodes. Conductance of the wire was found to vanish after dimerization. de Maria and Springborg arrived at the same conclusion for an infinite wire of Au atoms [11]. Sanchez-Portal *et al.* [12] found only a very small Peierls gap in their studies on finite Au wires in the large inter-atomic spacing limit, and argued that this instability would play no substantial role in the properties of Au wires. More recently, Ribeiro and Cohen [13] have studied infinite monatomic wires of Au, Al, Ag, Pd, Rh and Ru. They concluded that for each of these systems, there is a range of inter-atomic distances over which a linear wire is stable.

Many of the materials studied so far are complex in certain respects. Aluminum has three valence electrons per atom, while for the  $5d$  elements, relativistic effects and spin-orbit interactions are important. A much simpler, and in fact, an ideal system to study Peierls instability is a wire of sodium atoms. Sodium is a simple *sp* metal with one valence electron per atom. Hence, according to Peierls's argument, one would expect that a dimerization of its structure will lower energy.

In this letter we examine the issue of Peierls instability in a 1D atomically thin infinite wire of Na atoms. We find that there is a regime of inter-atomic distances where a wire of Na atoms does not have a Peierls or spin-Peierls instability, and has a stable uniform linear structure with metallic band structure. At lower interatomic distances, it develops a zigzag distortion but remains metallic. At higher interatomic distances it undergoes a *very weak* Peierls transition just before breaking. Most significantly, we show that whether a uniform Na wire has a Peierls instability or not can be rationalized in terms of its electron-phonon coupling properties. To our knowledge, this is the first independent confirmation from first-principles of results obtained in calculations with model Hamiltonians.

First-principles calculations of Na wires are performed within density functional theory (DFT). The wires are treated within a supercell geometry. The wire length is taken to be along the  $z$  direction. In order to reduce interactions between a wire and its periodic images

in our calculations, the lengths of the periodic box along  $x$  and  $y$  are taken to be 20 Å each. Wavefunctions were expressed in terms of plane waves with an energy cutoff of 450.0 eV. Potential due to the atomic cores are represented by Troullier-Martins pseudopotential. In most of our calculations the exchange-correlation effects have been treated within local density approximation (LDA) or local spin-density approximation (LSDA). In a few cases we have treated these within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA). Unless mentioned specifically, all results refer to LDA/LSDA calculations. The Brillouin Zone (BZ) integrations were performed within Monkhorst-Pack (MP) scheme. For ground state electronic structure and geometry calculations, a  $(1 \times 1 \times 8)$   $\mathbf{k}$ -point grid was used. We checked for convergence of total energy with respect to the size of the grid.

Phonon band structure and electron-phonon coupling are calculated within density functional perturbation theory (DFPT). For electron phonon calculations, very accurate knowledge of the Fermi surface is required, and usually a much finer  $\mathbf{k}$ -point grid is necessary. For this, we used a  $(1 \times 1 \times 24)$   $\mathbf{k}$ -point grid. Phonon band structure was obtained by interpolating from energies calculated at 8  $\mathbf{k}$ -points. For calculating electron-phonon coupling strength of bulk Na metal we used a  $(20 \times 20 \times 20)$  MP  $\mathbf{k}$ -point grid, while the phonon band structure was interpolated from explicit energy calculations on a  $(4 \times 4 \times 4)$   $\mathbf{k}$ -point grid. All the numerical calculations are performed with the ABINIT code.

Fig. 1 plots the total energies of three different 1D structures of Na atoms as a function of inter-atomic distance. Structure **L** is a uniformly spaced linear wire of Na atoms. **W** and **T** are two different zigzag structures. The low-energy **T** structure has a bond angle of  $\sim 60^\circ$ , so that three neighboring Na atoms form an equilateral triangle. Another way of looking at the **T** structure is as if two parallel uniform linear wires are displaced by half lattice spacing along the length of the wire. The **W** structure, on the other hand, has one bond angle that is obtuse at intermediate  $d$  values, and changes with  $d$ . In the **T** structure, each Na atoms has four nearest neighbors (NN), while in the **W** structure, the number of NN's is two. Presumably, it is this greater number of NN's that gives the **T** structure a greater stability.

The **L** wire has an optimum bond length of  $d = 3.3$  Å. However, the **W** and **T** structures are more favorable energetically compared to the **L** structure at this, and lower values of  $d$ . It is interesting to compare the behavior of a Na wire with those of other elements. At lower values of  $d$ , monatomic wires of all elements studied so far develop zigzag distortions [8, 9,

12, 13, 14]. Of these, only Al and Au wires have a metastable **W** structure. For all other elements, a **W** wire transforms to a **T** wire without any energy barrier. In wires of Ca and K, zigzag distortions set in exactly at the optimum bond length of an **L** wire [14]. However, as seen in Fig. 1, a uniform Na wire distorts to a zigzag **W** wire at  $d = 3.4$  Å, even before it reaches its optimum bond length. In this respect a Na wire is similar to a Cu wire [14]. That a Na wire behaves similar to a Cu wire, and is different from a K wire is rather surprising, and the reason is not immediately clear.

Why the **L** structure spontaneously distorts to a **W** structure at intermediate values of  $d$  can be understood from its phonon properties. Any structural instabilities of the **L** wire will show up as soft modes in its phonon band structure. Peierls instability is one such possibility which would be signaled by softening of a longitudinal mode at the zone boundary. Fig. 2 shows the phonon band structure of the uniform **L** wire at its equilibrium structure  $d = 3.3$  Å. We find one longitudinal and two soft transverse modes. Eigenvectors of the transverse modes indicate that they correspond to zigzag distortions of the linear wire. There are two orthogonal directions perpendicular to the wire length in which zigzag distortions can take place. This makes the mode doubly degenerate. This indicates that the **L** wire will spontaneously deform into a zigzag structure. Importantly, there is no indication of a Peierls instability in the phonon band structure of the **L** wire.

Though there were no indications of a Peierls instability in the phonon spectrum of the uniform **L** wire, we did an explicit search for a PI phase by dimerizing the uniform wire by hand at  $d = 3.3, 3.65, 3.8$  and  $3.9$  Å. This is an independent check of what is already seen in the phonon spectrum calculated via DFPT methods. As a test of our calculations, we reproduced the spin-Peierls ground state of an Al wire at  $d = 5.6$  Å as reported in Ref. [8], with energy gain over a uniform paramagnetic wire in excellent agreement with this work.

Fig. 3 shows the results of our calculations for longitudinally dimerized linear wires at the four  $d$  values mentioned. The longitudinal distortion in the uniform wire has been quantified by the parameter  $\Delta$ , which is equal to the separation of the two dimerizing atoms normalized by  $d$ .

At  $d = 3.3$  Å, as well as at  $d = 3.65$  Å, increasing the magnitude of longitudinal distortion monotonically increases the total energy of the wire. At very small distortions, the increase in energy we find is beyond the limit of accuracy of our DFT calculations. However, the trend is very clear, and by  $\Delta = 0.02$ , the energy difference with the uniform wire become

significant. This clearly shows that the dimerized structure is not the ground state of a Na wire at these  $d$  values. However, at  $d = 3.8$  Å, there is a small decrease in energy due to dimerization over a range of  $\Delta$ . With further increase in  $\Delta$ , the energy eventually increases. This signifies that the wire has an optimally dimerized stable structure. The maximum energy gain we find in our LDA calculations is  $\sim 1$  meV/atom. We have repeated this calculation using GGA. The energy gain increases marginally to  $\sim 2$  meV/atom. Although the calculated energy gains are very small, and are barely at the limit of these calculations, we believe this may be taken as a reasonable indication for a PI ground state. This claim is supported by the phonon band structure of the linear wire at  $d = 3.8$  Å as discussed later. This shows that a Na wire will undergo a Peierls transition only at large inter-atomic separations, and that this instability is *very weak* in that the energy gained by dimerization is very small. Moreover, there is a regime of  $d$  where the wire is stable in a uniform **L** structure. Interestingly, at  $d = 3.9$  Å, the energy steadily decreases with increasing distortion over the range of  $\Delta$  we have studied. Contrasting this with its behavior at  $d = 3.8$  Å, this is an indication that the wire will break into isolated dimers at  $d = 3.9$  Å.

Though not the ground state at  $d = 3.3$  and  $3.65$  Å, a dimerized structure, nonetheless, has two valence electrons per unit cell, and one would expect it to be an insulator. This is borne out by our calculations. Fig. 4 shows the band structures of a uniform **L** wire, a dimerized linear wire at  $\Delta = 0.01$  (both around  $d = 3.3$  Å), and the **T** wire in its equilibrium structure at  $d = 1.74$  Å. To make comparison easier, the bands of the uniform **L** wire have been folded onto half of the BZ. The uniform wire is metallic with a half-filled band, as one would expect. The gap opening due to dimerization is clearly seen in the band structure of the distorted linear wire. Magnitude of the band gap increases with increase in distortion,  $\Delta$ . Interestingly, the **T** structure is also metallic, though it also has two valence electrons per unit cell, and naively one would expect it to be an insulator. It was shown long ago by Batra [15] that zigzag distortions of a 1D metallic system, leading to a doubling of the unit cell, do not open gaps in their electronic spectrum. It is only the longitudinal distortions which open gaps. Our calculation is another example of this fact.

In order to understand better the structural instabilities of the **L** wire in the large  $d$  regime, we calculated its phonon band structure at  $d = 3.8$  Å, which is shown in Fig. 5. There is one soft mode in this case near the zone boundary. From the phonon eigenvectors it is seen to be a longitudinal mode, which indicates that the uniform **L** wire, in fact, has a

Peierls instability at this  $d$ . It is also interesting to note that the transverse modes giving zigzag distortions of the wire are not soft at this  $d$ . Consequently, there is no instability towards zigzag distortions, something we have already seen (Fig. 1).

We also searched for anti-ferromagnetic (AFM) and spin-Peierls phases in a Na wire. Though an  $sp$  element like Na is not expected to, and does not show any magnetic ordering in 3D bulk, it is not completely unexpected for such elements to show magnetic order at low coordination. In fact, as we have already mentioned, an Al wire was found to have a spin-Peierls ground state. We looked for an AFM solution in a uniform  $\mathbf{L}$  wire at  $d = 3.3, 3.65, 3.8$ , and  $3.9 \text{ \AA}$ , and also looked for spin-Peierls solutions at these  $d$  values. The wires always converged to spin unpolarized states, thus explicitly confirming that there are no AFM or spin-Peierls instabilities in a 1D Na wire.

We now try to rationalize why a 1D Na wire has a Peierls instability only at large values of  $d$ . For this we wish to recall a number of calculations that have been performed on 1D lattice models in the context of Peierls transition [16, 17, 18]. The three models relevant to our discussions here are the 1D Holstein model for spin-less Fermions, the same model for spin- $\frac{1}{2}$  fermions, and the Hubbard-Holstein model. A major conclusion from studies on all these models is that a 1D metallic system undergoes a Peierls transition only if the coupling of the electrons to phonons is larger than a threshold. While it is not possible to quantitatively compare values of the parameters in these lattice models and our first-principles calculations, we think that an explanation of the absence of a Peierls transition at smaller values of  $d$  may still lie in the electron-phonon coupling strength in the wire.

Electron-phonon properties of the wires have been calculated within Migdal theory (MT). A detailed discussion on MT can be found in Ref. [19]. Whether MT is applicable to strictly 1D systems is not clear. However, the formalism we have used treats the simulation system as 3D, with vacuum surrounding the atomically thin Na wires. In fact, MT has been applied for calculation of electron-phonon properties in similar wires [20] of Al within the same plane-wave DFT formalism. Within MT, a measure of the electron-phonon coupling is the ‘electron-phonon spectral function’ denoted by  $\alpha^2F(\Omega)$ . This is a measure of the effectiveness of phonons of frequency  $\Omega$  in scattering electrons from any state to any other state on the Fermi surface. Figs. 2 and 5 show  $\alpha^2F(\Omega)$  for a uniform  $\mathbf{L}$  wire at  $d = 3.3 \text{ \AA}$  and  $d = 3.8 \text{ \AA}$  respectively, as a function of phonon energy. It is clear that the electrons primarily couple to the longitudinal phonon, and that the coupling is more than three times

TABLE I: Calculated and experimental  $\lambda$ 's for bulk Na metal and **L** wires

System	Calc.	Expt.
Na bulk	0.23	0.22 <sup>a</sup>
<b>L</b> wire( $d=3.3$ Å)	0.01	–
<b>L</b> wire( $d=3.8$ Å)	0.16	–

<sup>a</sup>Ref. [21]

larger at  $d = 3.8$  Å compared to that at  $d = 3.3$  Å. Along with electron-phonon coupling strength,  $\alpha^2 F(\Omega)$  also depends on the phonon density of states. Averaging over the phonon density of states, the mass enhancement parameter  $\lambda$  is used as a more direct measure of the electron-phonon coupling strength.  $\lambda$  is defined to be the first inverse moment of  $\alpha^2 F(\Omega)$ :

$$\lambda = 2 \int_0^\infty \frac{d\Omega}{\Omega} \alpha^2 F(\Omega). \quad (1)$$

We have calculated  $\lambda$  for the uniform **L** wires at  $d = 3.3$  Å, and  $d = 3.8$  Å. For comparison, we have also calculated its value for bulk Na metal at the optimal lattice constant calculated within LDA.

Table I shows our calculated values of  $\lambda$  along with the experimental value for the bulk system. This clearly shows that the strength of electron-phonon coupling in the 1D **L** wire at  $d = 3.3$  Å is small compared to the bulk system. More significantly,  $\lambda$  increases by an order of magnitude as  $d$  increases from 3.3 Å to 3.8 Å. We believe, it is this increase in electron-phonon coupling which drives a Na wire to a PI at large values of  $d$ 's.

In conclusion, we have shown that a monatomic wire of Na atoms has a stable uniform linear structure over a range of inter-atomic distances. Below 3.4 Å, it distorts to a wide-angled zigzag structure which eventually transforms to an equilateral triangular structure on further compression. On stretching the wire it breaks at  $d \sim 3.9$  Å. Before that, at  $d \sim 3.8$  Å, it has a PI ground state. However, the Peierls instability in a Na wire is very weak, as the energy gain on dimerization is very small. We rationalize the existence or non-existence of a PI ground state in terms of the electron-phonon coupling strength in the wire. We also speculate that the observed stable uniform linear structures of Au, Al, Ag, Pd, Rh, and Ru over a window of inter-atomic distances [13] may have the same explanation.

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Tipu cluster at HRI.

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## Figure Captions

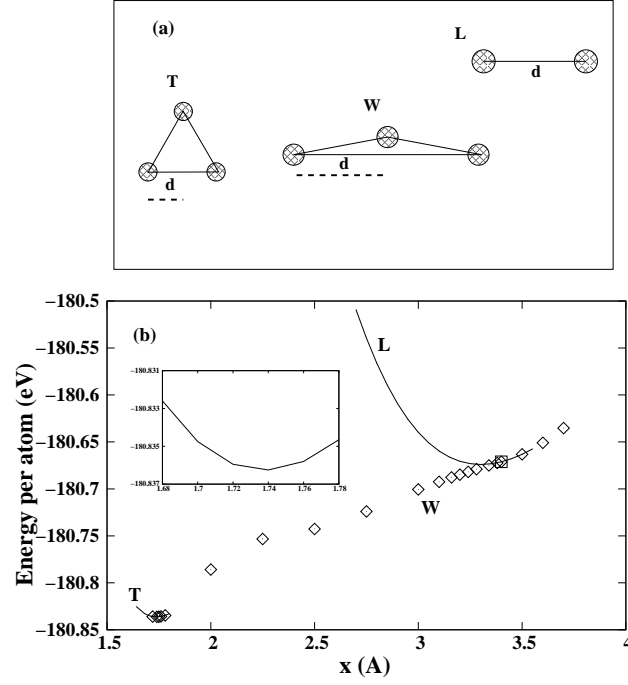


FIG. 1: (a) Geometries of three different 1D wires of Na atoms studied in this work. (b) Variation of total energy per atom as a function of interatomic distance for **L** (solid line), **W** (diamond), and **T** (solid line) wires. The inset shows the energy variation of the **T** wire with  $d$ .

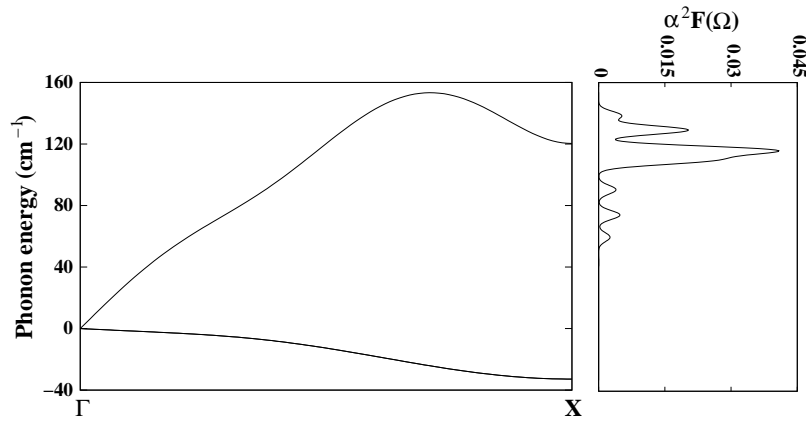


FIG. 2: Phonon band structure and electron-phonon spectral function of a **L** wire of Na atoms at  $d = 3.3$  Å.

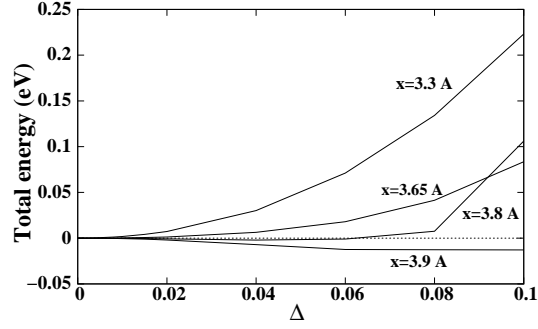


FIG. 3: Total energy of the **L** wire as a function of longitudinal distortion  $\Delta$  for different  $d$  values. In all cases, energy of a uniform wire has been taken as zero which is denoted by the dotted line.

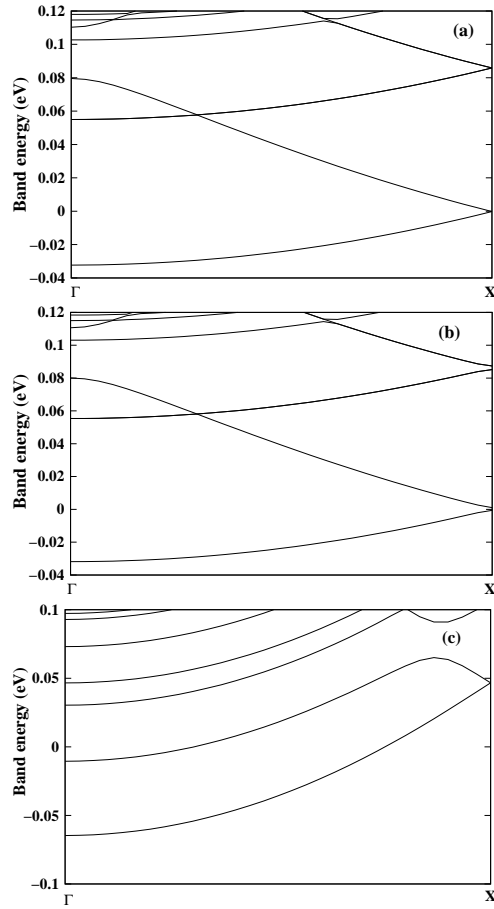


FIG. 4: Electronic band structures for a uniform **L** (a), dimerized **L** at  $\Delta = 0.01$  (b), and **T** wire (c) of Na atoms. The bands of the uniform **L** wire are folded for easy comparison. The Fermi energy has been set equal to zero in all cases.

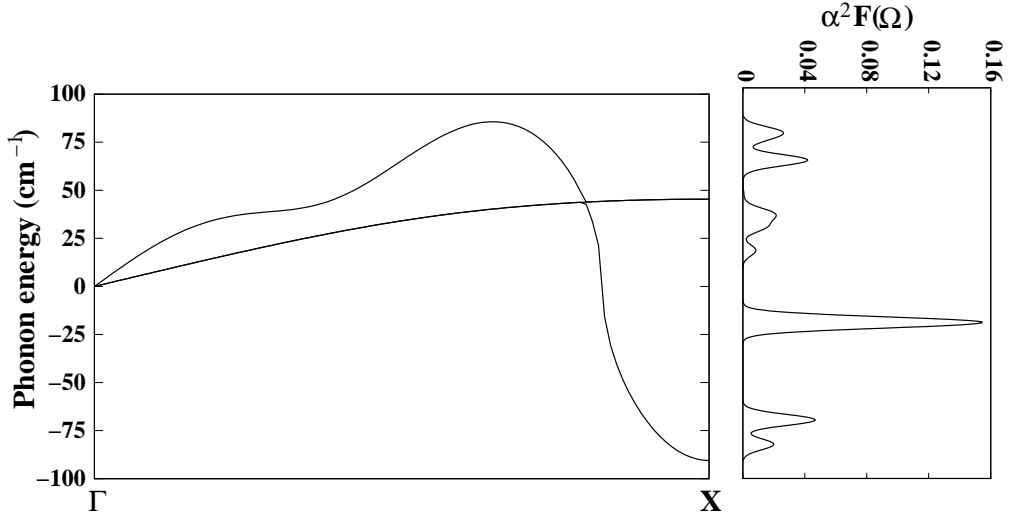


FIG. 5: Phonon band structure, and electron-phonon spectral function for a uniform  $\mathbf{L}$  wire at  $d = 3.8 \text{ \AA}$ .